

## REMARKS

In the Office Action dated June 13, 2003, Claims 2-8, 10, 11 and 13 are pending and under consideration. The Examiner has rejected claims 7 and 13 as allegedly indefinite under 35 U.S.C. 112, second paragraph. Claims 2, 3, 7 and 13 have been rejected as allegedly anticipated by Hermann et al. (U.S. Patent No. 3,477,986) under 35 U.S.C. 102(b); claims 4, 5, 6 and 10 have been rejected as allegedly unpatentable under 35 U.S.C. 103(a) over Hermann et al. (U.S. Patent No. 3,477,986) and further in view of Watanabe et al. (U.S. Patent No. 5,266,618), Gijsman (EP 390,277), Lee (U.S. Patent No. 3,865,792) and Rody et al. (U. S. Patent No. 4,200,026). Claims 8 and 11 have been rejected as allegedly unpatentable under 35 U.S.C. 103(a) over Hermann et al. (U.S. Patent No. 3,477,986) and further in view of Rody et al. (U. S. Patent No. 4,200,026).

This response addresses each of the Examiner's rejections. Applicants respectfully submit that the present application is in condition for allowance. Favorable consideration of all pending claims is respectfully requested.

Claims 7 and 13 are independent. Claims 7 and 13 have been amended to incorporate the elements of the dependent claims 2-6 and 10-11. Claims 2-6 and 10-11 have been cancelled, without prejudice. Support for these amendments is found throughout the specification and, for example, at page 4, lines 22-28; page 5, lines 2-6 and 28-32; and page 6, lines 1-2. No new subject matter has been added by this amendment.

Claims 7 and 13 have been rejected under 35 U.S.C. §112, second paragraph, as allegedly indefinite. In response, Applicants respectfully submit that PACM-12 and PPD-T are well known in the literature. It is well accepted to use letters instead of numbers to designate certain monomers, e.g., abbreviations such as PACM. The abbreviations stand for long names and descriptions. For example, PACM stands for 4,4'-diaminodicyclohexylmethane and PPD-T stands for poly p-phenyleneterephthalamide. Applicants respectfully direct the Examiner's attention to Ullman's Encyclopedia of Industrial Chemistry, vol. A21, pp. 179-181 (attached herewith as **Exhibit 1**), which describes the PACM; and to Fiber Types ([http://www.eng.uab.edu/compositesLab/b\\_fiber.htm](http://www.eng.uab.edu/compositesLab/b_fiber.htm), attached

herewith as **Exhibit 2**), which describes PPD-T. Accordingly, Applicants respectfully request the withdrawal of the rejection of claims 7 and 13 under 35 U.S.C. §112, second paragraph.

Claims 2, 3, 7 and 13 have been rejected as allegedly anticipated by Hermann et al. (U.S. Patent No. 3,477,986) under 35 U.S.C. § 102(b). Herman et al. disclose phosphonium halides, which are ionic in nature. In stark contrast, the compounds of the present invention are covalent compounds and are distinct. Applicants respectfully submit that Hermann et al. do not anticipate the claims as recited. Applicants respectfully request withdrawal of the rejection of claims 2, 3, 7 and 13 under 35 U.S.C. 102(b).

Claims 2, 3, 7 and 13 have been rejected as allegedly unpatentable under 35 U.S.C. § 103(a) over Hermann et al. Hermann et al. teach certain copper compounds and halogen-containing aromatic and aliphatic ionic phosphonium compounds and do not teach or suggest any halogen containing covalent compounds in combination with copper compounds. Accordingly, Hermann et al. do not suggest, or motivate a person in the art to make, a polyamide composition as claimed in the present invention. In addition, Applicants respectfully direct the attention of the Examiner to a detailed discussion in the specification distinguishing the halogen salt stabilized prior art compounds from the covalent halogen stabilized compounds of the present invention (see the specification, for example, at page 6, line 30 – page 7, line 16). The polymers of the present invention containing covalent halogen compounds show improved long term temperature stability, improved tracking resistance and lower discoloration. These advantages of the present invention are due to the presence of organic halogen containing covalent compounds. Accordingly, Hermann et al. do not suggest, or provide motivation to make, the present invention to a person of ordinary skill in the art. Applicants respectfully request withdrawal of the rejection of Claims 2, 3, 7 and 13 under 35 U.S.C. § 103(a).

Claims 4, 5, 6 and 10 have been rejected as allegedly unpatentable under 35 U.S.C. § 103(a) over Hermann et al. and further in view of Watanabe et al. (U.S. Patent No. 5,266,618), Gijsman (EP 390,277), Lee (U.S. Patent No. 3,865,792) and Rody et al. (U. S. Patent No. 4,200,026). The Examiner alleges that it would have been obvious to add to the moldings of Hermann et al., the phosphates of Watanabe et al. for imparting flame retardency and impact strength; the halogen substituted compounds of Gijsman for stabilization; the

chloroparaffin of Lee to enhance flame retardancy; and organic phosphites of Rody et al. to impart a synergistic effect in stabilization.

Hermann et al. has been fully distinguished above. In this regard, none of the secondary references cited by the Examiner overcome the deficiencies of the primary reference. Accordingly, the rejections of claims 4, 5, 6 and 10 are overcome and withdrawal thereof is respectfully requested.

Watanabe et al. teach a resin composition comprising a thermoplastic resin, a phosphorous compound, a boron compound and a polyorganosilane compound. Watanabe et al. suggest that the resin could be either a polycarbonate or a mixture of polycarbonate and non-polycarbonate polymers. However, Watanabe et al. do not suggest or teach 100% non-polycarbonate polymer. In addition, Watanabe et al. do not teach or suggest or motivate a person of ordinary skill in the art to replace both organosilane and boron compounds by a copper compound as in the present invention. Accordingly, Watanabe et al. do not teach or suggest, or provide motivation to a person of ordinary skill in the art, to make the present invention.

Rody et al. teach polymers, which contain sterically hindered polyalkylpiperidine groups and organic phosphates. Rody et al. describe that polyalkylpiperidines show surprising light stabilization of plastics (see Rody et al., column 1, line 35 – column 2, line 28). Thus, according to Rody et al., without a polyalkylpiperidine polymer or oligomer as a stabilizer, there cannot be light stabilization of plastics. Rody et al. suggest the use of other light stabilizers or organic phosphites in addition to polyalkylpiperidines stabilizers for synergistic effect. However, Rody et al. do not teach or suggest or motivate a person of skill in the art to substitute a light stabilizing polyalkylpiperidine oligomer or polymer with copper or phosphate compounds as presently claimed. In addition, Applicants reiterate their argument with regard to the distinction between light stabilization and heat stabilization. That heat stabilizers, e.g. thermal stabilizers, are separately categorized from UV stabilizers, which is synonymous with ultraviolet light stabilizers and establishes the clear line of distinction between heat and light stabilizers (see Modern Plastics Encyclopedia '90, pages 204, 206, and 209-211, submitted with previous response). Accordingly, Rody et al. do not teach or suggest the present invention or provide motivation to a person of ordinary skill in the art to make the present invention.

Gijsmann discloses a copper-stabilized polyamide 4.6 composition, especially a combination of a water insoluble copper salt in a very low concentration, a halogen substituted organic compound and polyamide 4.6. The Gijsman reference, limited as it is to a composition which includes copper stabilized polyamide 4.6 and stabilized only under extreme high processing conditions, bears no resemblance to the claimed composition, which is characterized by the polyamides of the type processed at lower temperatures, in the range of about 220°C to about 270°C, such as polyamide 6 and polyamide 66. Indeed, the teaching of Gijsman emphasizes that special stabilizing copper compounds must be utilized in view of the high temperature processing of polyamide 4.6. Thus, one skilled in the art would not look to the special requirements, associated with the use of polyamide 4.6, in the stabilization of the polyamide compositions claimed herein.

Lee discloses that fire retardant materials such as chloroparaffins may be used with a polyamide. The present invention does not aim at improving fire retardancy but aims at providing a polyamide composition having a good aging stability combined with improved electric properties (see the detailed explanation in the application and the experiments as provided in the specification, e.g., page 13-23). Accordingly, Lee does not disclose any copper additives or teach, suggest, or provide motivation to a person of ordinary skill in the art, to make the present invention.

Obviousness cannot be established by combining the teachings of the prior art to produce the claimed invention, absent some teaching, suggestion or incentive supporting the combination. *ACS Hospital Systems, Inc. v. Monteffiore Hospital*, 732 F. 2d 1572, 1577, 221 USPQ 929, 933 (Fed. Cir. 1984). The mere fact that references can be combined or modified does not render the resultant combination obvious unless the prior art also suggests the desirability of the combination. *In re Mills*, 916 F. 2d 680, 16 USPQ2d 1430 (Fed. Cir. 1990). The rejection of claimed subject matter under 35 U.S.C. §103 in view of a combination of references requires that the suggestion to carry out the claimed invention must be found in the prior art, not in Applicants' disclosure. Hence, Applicants respectfully submit that there is no motivation to combine these references to arrive at the present invention as presently claimed. Thus, the combination or modification of the prior art references as contemplated by the Examiner is overcome and Applicants respectfully request withdrawal of rejection of claims 4, 5, 6, and 10 under 35 U.S.C. § 103(a).

Claims 8 and 11 have been rejected as allegedly unpatentable under 35 U.S.C. 103(a) over Hermann et al. (U.S. Patent No. 3,477,986) and further in view of Rody et al. (U.S. Patent No. 4,200,026).

The Examiner acknowledges that Hermann et al. do not suggest the claimed master batch of instant claim 8 or the phosphorous compound of instant claim 11. However, the Examiner alleges that it would have been obvious to use a master-batch of copper salt and an organic halogen compound in order to control the addition of small amounts precisely.

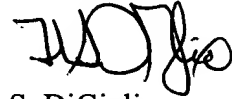
Hermann, et al. have been distinguished above. Rody et al. fail to ameliorate the deficiencies of the primary reference. Therefore, the rejection of claims 8 and 11 are overcome and withdrawal thereof is respectfully requested.

Allegedly, it would also have been obvious to add the organic phosphites of Rody et al. to the moldings of Hermann et al., for stabilization. Nowhere in Rody et al. is it disclosed that copper compounds could be used as additives along with phosphites in polyamide polymers. Hermann et al. do not disclose any of the moldings of the present invention. There is no motivation to combine these references to arrive at the present invention as claimed. As mentioned above, the rejection of claimed subject matter under 35 U.S.C. §103 in view of a combination of references *requires* that the suggestion to carry out the claimed invention must be found in the prior art, *not in Applicants disclosure*.

With regard to method claims 7, 8 and 11, the Examiner further alleges that mixing is a well-known and quite a common step in the preparation of a composition. It is well known in the art that many preparations involve mixing of two or more substrates and reagents. Yet, new methods of preparation of compositions are discovered involving the same mixing method. Applicants respectfully submit that the methods claimed are not just mixing, but mixing certain substrates as presently claimed; and the claimed combination is not provided by the cited art. Accordingly, the rejections of claims 7, 8, and 11 are overcome and withdrawal thereof is respectfully requested.

Thus, in view of the foregoing, it is firmly believed that the present application is in condition for allowance, which action is earnestly solicited.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'F. DiGiglio', written over the printed name.

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## **EXHIBITS**

1. Ullman's Encyclopedia. of Industrial Chemistry, vol A21, pp. 179-181
2. Fiber Types ([http://www.eng.uab.edu/compositesLab/b\\_fiber.htm](http://www.eng.uab.edu/compositesLab/b_fiber.htm))

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## Polyamides

General aspects of polymers, properties and testing, processing, additives, and analysis are discussed in *Plastics, General Survey*; *Plastics, Properties and Testing*; *Plastics, Processing*; *Plastics, Additives*; and *Plastics, Analysis*, respectively. States of order are treated in *Plastics, Properties and Testing*. Fundamental aspects of polymerization reactions are treated in *Polymerization Processes*.

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## 1. Introduction

Polyamides are, literally, polymers that contain an amide group,  $-\text{CONH}-$ , as a recurring part of the chain. The polyamides known as "nylons" exclude (1) the proteinaceous polyaminoacids, (2) the relatively low-melting "polyamide resins" used in inks, adhesives, and coatings ( $\rightarrow$  Resins, Synthetic) and (3) the wholly aromatic "aramids" used to make high-performance fibers ( $\rightarrow$  High-Performance Fibers, A 13, pp. 12–17). Rate and equilibrium constants, thermal and oxidative stability, resistance to hydrolysis and solvents, and other chemical behavior depend on the specific polymer, but the basic chemistry discussed herein applies to all of these polyamides.

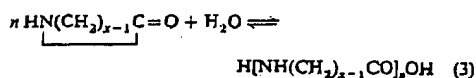
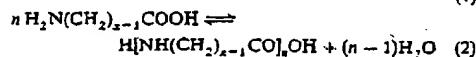
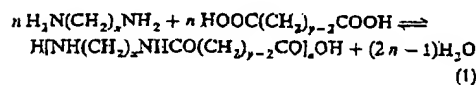
**History.** The year 1929 saw the publication of the original papers of CAROTHERS [1], [2] on polycondensation which gave incontrovertible evidence to the Staudinger thesis [3] that polymers are high molecular mass species and not aggregated entities. CAROTHERS' classic review of polymerization and definition of terminology still valid today appeared in 1931 [4]. Development of techniques to achieve molecular masses in excess of 10000 led to realization of the potential for fiber formation. This was the genesis of the effort by the Du Pont company which yielded "nylon": the first semicrystalline polymer, the first synthetic fiber, and the first engineering thermoplastic. The term "nylon" is generic and is equivalent to "polyamide" in the limited sense defined above. Synthesis of poly(hexamethylene adipamide), the original "nylon", in a Du Pont laboratory in 1935 provided a material whose properties were judged to be appropriate for apparel use and culminated in its commercial introduction in 1938. The other principal polyamide or nylon, polycaprolactam, was first made in an IG Farben laboratory by SCHLACK in 1938. The history of these nylons and those made from 11-aminoundecanoic



acid and dodecanolactam were reviewed in 1986 [5]–[7]. Although use as a fiber dominated the interest in nylon from the outset, application as a plastic for a variety of purposes such as brush filaments, wire coating, coil forms, and gears occurred very soon thereafter. The use of nylons as plastics has steadily increased versus that of fibers. In the United States it has gone from 7% in 1965 to 11% in 1978 and 22% in 1988; in Western Europe, from 24% in 1978 to 47% in 1988. Economic aspects are reviewed in Chapter 9. For a discussion of polyamides used as fibers, see → Fibers, 4. Synthetic Organic, A10, pp. 569–579. The focus of this article is on the polyamides used as plastics.

### 1.1. Nomenclature

The nylons (polyamides) under discussion here are most often made from (1) diamines and dibasic acids, (2)  $\omega$ -amino acids, or (3) lactams:



Equation (3) represents the hydrolytic polymerization of a lactam. It is described in detail in Section 2.2.

Where two types of reactive monomer are required, the polymerization is said to be an

AABB type; where one suffices, an AB type. A and B stand for the functional groups  $-\text{NH}_2$  and  $-\text{COOH}$ , respectively. In current practice AABB and AB may describe products that do not involve polymerization via amine and acid ends but can be visualized as if so made. This is realistic because the same equilibria in the presence of water or other solvolytic agents will apply.

Useful molecular mass requires better than 99% reaction and places a high demand on purity of the reactants. Stoichiometry is also critical for AABB types. The AABB types are regarded as homopolymers because of the absolute need for alternation of both reactants to form a polymeric chain which includes both moieties in the repeating structure (see Chap. 2). This is consistent with IUPAC recommendations [8]. Copolymers result from simultaneous polymerization of AABB and AB types or use of more than one AA, BB, or AB type. They are common and were used as early as 1940 [6].

The polyamides (PA) or nylons are identified by numbers corresponding to the number of carbon atoms in the monomers (diamine first for the AABB type).

Table 1 provides a list of the common names of the commercial nylon homopolymers, their numerical designations, their CAS registry numbers, and their CAS names. The systematic IUPAC naming of polyamides [9] is awkward and is rarely encountered in the commercial literature.

Table 1. Commercial polyamides or nylons

Common name	xy or x*	CAS name, CAS registry no.
Poly(tetramethylene adipamide)	46	poly[imino(1,4-dioxo-1,4-butanediyl)imino-1,6-hexanediyl] [24936-71-8]
Poly(hexamethylene adipamide)	66	poly[imino(1,6-dioxo-1,6-hexanediyl)imino-1,6-hexanediyl] [32131-17-2]
Poly(hexamethylene azelaamide)	69	poly[imino-1,6-hexanediylimino(1,9-dioxo-1,9-nonanediyl)] [28757-63-3]
Poly(hexamethylene sebacamide)	610	poly[imino-1,6-hexanediylimino(1,10-dioxo-1,10-decanediyl)] [9008-66-6]
Poly(hexamethylene dodecanoamide)	612	poly[imino-1,6-hexanediylimino(1,12-dioxo-1,12-dodecanediyl)] [24936-74-1]
Poly(dodecamethylene dodecanoamide)	1212	dodecanedioic acid, polymer with 1,12-dodecanediamine [36497-34-4]
Poly(m-xylylene adipamide)	MXD 6	poly[iminomethylene-1,3-phenylene-methylenecimino(1,6-dioxo-1,6-hexanediyl)] [25805-74-7]
Poly(trimethylhexamethylene terephthalamide)	TMDT	1,4-benzenedicarboxylic acid, polymer with 2,2,4-trimethyl-1,6-hexanediamine and 2,4,4-trimethyl-1,6-hexanediamine [25497-66-9]
Poly(11-aminoundecanoamide)	11	poly[imino(1-oxo-1,11-undecanediyl)] [25035-04-5]
Polycaprolactam or polycaproatamide	6	poly[imino(1-oxo-1,6-hexanediyl)] [25038-54-4]
Polydodecanolactam or polylauroactam or polydodecanoamide	12	poly[imino(1-oxo-1,12-dodecanediyl)] [24937-16-4]

\* xy and x refer to the number of carbon atoms according to Equations (1)–(3).

Table 2. Monomers for polyamides

Common and (CAS) name	CAS registry no.	x or y*	Source	Properties and synthesis
Adipic acid (hexanedioic acid)	[124-04-9]	6	benzene, toluene	→ Adipic Acid
Azelaic acid (nonanedioic acid)	[123-99-9]	9	oleic acid	→ Dicarboxylic Acids, Aliphatic, A 8, p. 531
Sebacic acid (decanedioic acid)	[111-20-6]	10	castor oil	→ Dicarboxylic Acids, Aliphatic, A 8, p. 531
Dodecanedioic acid	[693-23-2]	12	butadiene	→ Dicarboxylic Acids, Aliphatic, A 8, p. 532
Dimer acid (fatty acids, dimers)	[61788-89-4]	36	oleic and linoleic acids	→ Dicarboxylic Acids, Aliphatic, A 8, p. 535
Isophthalic acid (1,3-benzenedicarboxylic acid)	[121-91-5]	1	m-xylene	→ Carboxylic Acids, Aromatic
Terephthalic acid (1,4-benzenedicarboxylic acid)	[100-21-0]	T	p-xylene	→ Terephthalic Acid
Tetramethylenediamine, 1,4-diaminobutane (1,4-butanediamine)	[110-60-1]	4	acrylonitrile and HCN	→ Amines, Aliphatic, A 2, p. 27
Hexamethylenediamine, 1,6-diaminohexane (1,6-hexanediamine)	[124-09-4]	6	butadiene, propene	→ Hexamethylenediamine
4,4'-Diaminodicyclohexylmethane (cyclohexanediamine, 4,4'-methylenebis-)	[1761-71-3]	PACM	aniline and formaldehyde	
m-Xylylenediamine (1,3-benzenedimethanediamine)	[1477-55-0]	MXD	m-xylene	
Trimethylhexamethylenediamine (mix of 1,6-hexanediamine, 2,2,4-trimethyl and 2,4,4-isomer)	2,2,4-[3236-53-1] 2,4,4-[3236-54-2]	TMD	acetone	
Dodecamethylenediamine, 1,12-diaminododecane (1,12-dodecanediamine)	[2783-17-7]	12	butadiene	→ Amines, Aliphatic, A 2, p. 27
11-Aminoundecanoic acid (undecanoic acid, 11-amino-)	[2432-99-7]	11	castor oil	
ε-Caprolactam (2-H-azepin-2-one, hexahydro)	[105-60-2]	6	benzene, toluene	→ Caprolactam
Laurolactam, dodecanolactam, (azocyclotridecane-2-one)	[947-04-6]	12	butadiene	→ Cyclodecanol, Cyclodecanone, and Laurolactam

\* x, y = number of carbon atoms according to Equations (1)–(3).

The CAS names are largely in accord with IUPAC practice, but examination of Table 1 reveals some inconsistencies. Many of the IUPAC rules for nomenclature are conveniently assembled in a polymer handbook [10] wherein, however, older versions of the IUPAC names for PA 66 and 6 are used [11]: poly-(iminoadipoyl-imino-hexamethylene) and poly[imino(1-oxohexamethylene)].

As shown in Table 1, it is sometimes necessary to use letters instead of numbers for certain monomers. The diamine TMD is a mixture of 2,2,4- and 2,4,4-trimethylhexamethylenediamine and yields head-to-head, head-to-tail isomerism in its polymer with, for example, terephthalic acid (T). Thus PA TMDT is, in fact, a copolymer. Another special case is PACM which is a mix of *cis-cis*, *cis-trans*, and *trans-trans* isomers. The crystallinity of the derived polymer and as-

sociated properties depend largely on the percentage of *trans-trans* isomer.

Pronunciation is in accord with the monomers so that 66 is six-six not sixty six, 612 is six-twelve, 11 is eleven, etc. Other nylons of commercial interest exist and will be discussed below where appropriate.

The monomers used in polyamide homopolymers and copolymers are listed in Table 2; *p*- and *m*-phenylenediamines could be added but are specific to the high-performance fibers. Included is dimer acid although its use is largely in the low-melting adhesive and ink resins.

## 2. Polyamidation

The basic concepts of equilibria and kinetics in polyamidation are in large measure due to

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# Fiber Types

● Glass Fibers

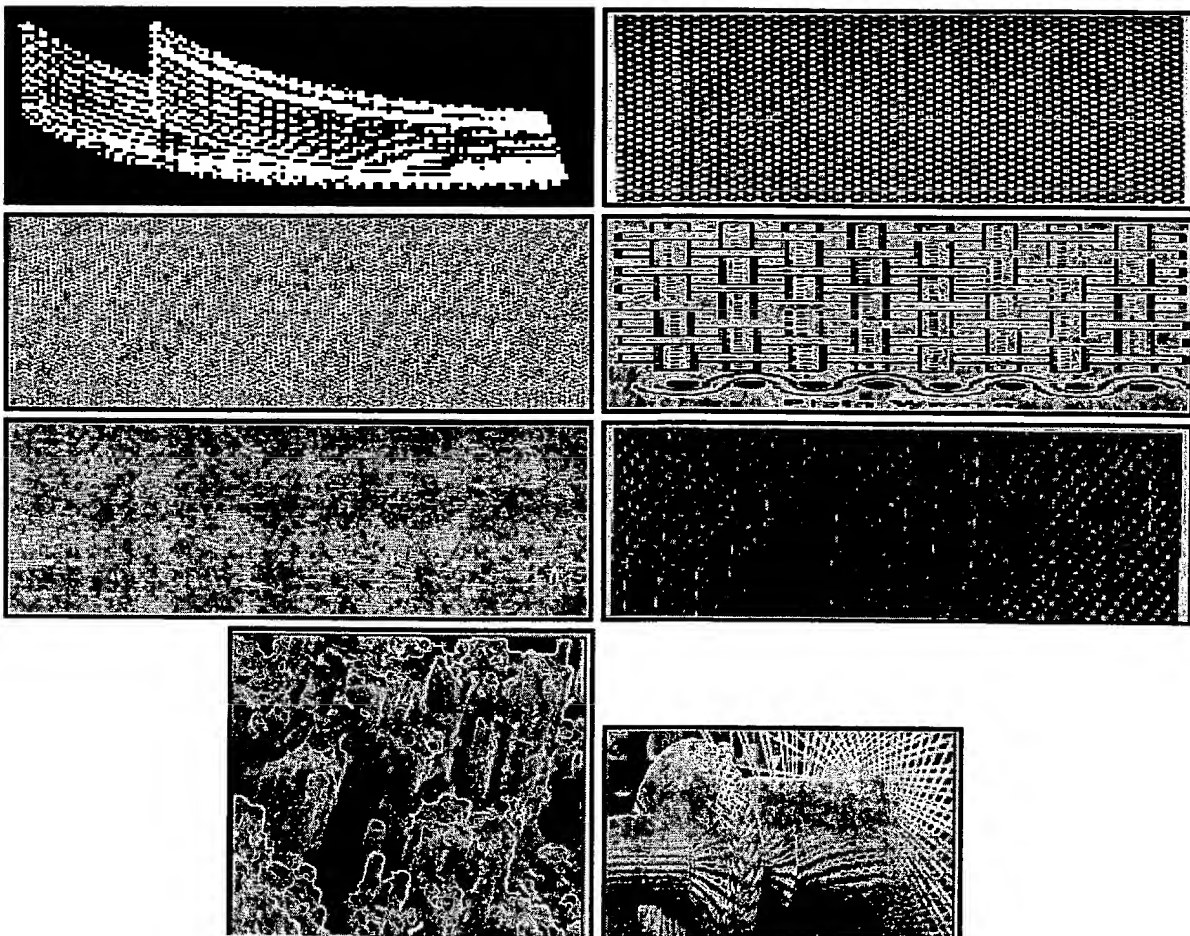
● Organic Fibers

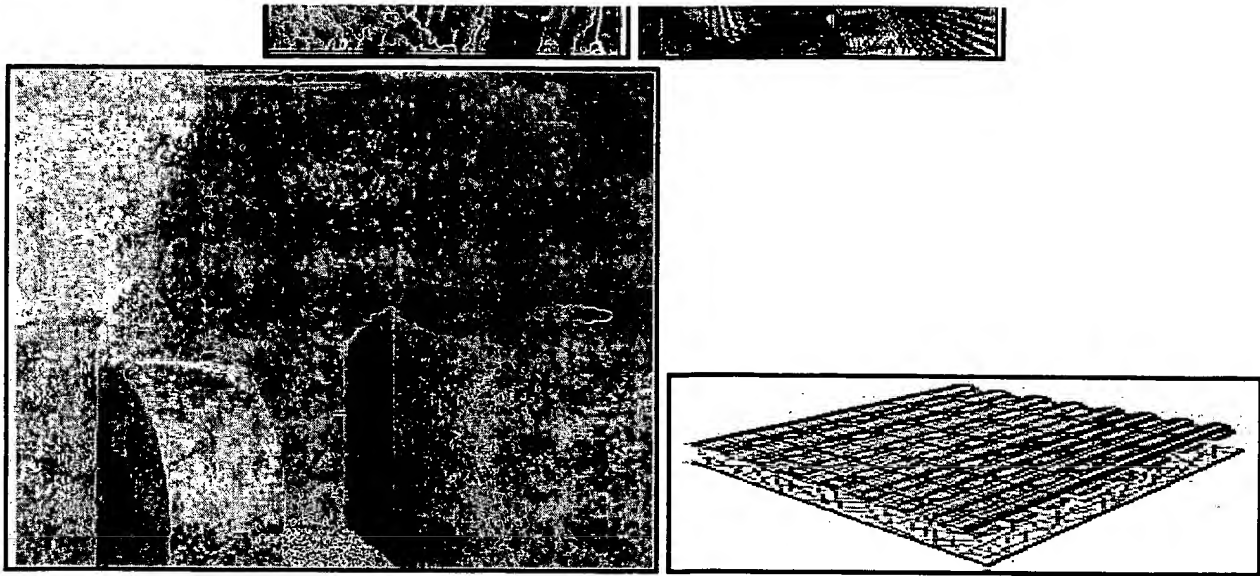
● Aramid Fibers

● Carbon Fibers

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## Glass Fibers

The most commonly used reinforcement material in fiber composites used in load bearing sandwich construction is the E-glass fiber. It has good mechanical properties and environmental resistance, but its competitiveness comes primarily from the relative low price. There are other types of glass reinforcement like S and R-glass with slightly better mechanical properties but their price are significantly higher at present time. The main ingredient in glass is  $\text{SiO}_2$ , about 50-70%, but other metal oxides are often added such as  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CaO}$ . The main drawback with glass reinforcement is that the elastic modulus is low and that the density is higher than for other reinforcements. Reinforcements need not necessarily be in the form of long fibers. One can have them in the form of particles, flakes, whiskers, discontinuous fibers, continuous fibers, and sheets. It turns out that the great majority of materials are stronger and stiffer in the fibrous form than in any other form, thus the great attraction of fibrous reinforcements. Specifically, in this category, we are most interested in the advanced fibers that possess very high strength and very high stiffness coupled with a very low density. The reader should realize that many naturally occurring fibers can and are used in situations involving not very high stresses. The great advantage in this case, of course, is that of low cost. The vegetable kingdom is, in fact the largest source of fibrous materials. Cellulosic fibers in the form of cotton, flax, jute, hemp, sisal, and ramie, for example, have been used in the textile industry, while wood and straw have been used in the paper industry. Other natural fibers, such as hair, wool, and silk, consist of different forms of protein. Glass fiber, in its various form, has been the most common reinforcement for polymer matrices. Kevlar (an aramid) fiber launched by Du Pont in the 1960s is much stiffer and lighter than glass fiber. Other high performance fibers that combine high strength with high stiffness are boron, silicon carbide, carbon, and alumina. These were all developed in the second part of the twentieth century. In particular, some ceramic fibers were developed in the 1970s and 1980s by a very novel method, namely the pyrolysis of organic precursors. The use of fibers as high performance engineering materials is based on three important characteristics:

Small diameter with respect to its grain size or other microstructural unit. This allows a higher fraction of the theoretical strength to be attained than that possible in a bulk form. This is a direct result of the so called size effect that is, the smaller the size, the lower the probability of having impurities in the material

A high aspect ratio. This allows a very large fraction of the load to be transferred via the matrix to the stiff and strong fiber

A very high degree of flexibility that is really a characteristic of a material having a high modulus and a small diameter. This flexibility permits a variety of techniques to be employed for making composites with these fibers. We first consider the concept of flexibility and then go on to describe importance of fibers in detail. Flexibility of a given material is a function of its elastic modulus and the moment of inertia of its cross section. The elastic modulus of a material is quite independent of its form or size. It is generally a constant for a given chemical

composition and density. Thus, for a given composition and density the flexibility of a material is determined by shape, size of the cross section and its radius of curvature which is a function of its strength.

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## Organic Fibers

In view of the fact that the covalent carbon-carbon bond is a very strong one, we should expect linear chain polymers such as polyethylene to be potentially very strong and stiff. What one needs for realizing this potential is full extension of molecular chains. The orientation of the polymer chains with respect to the fiber axis and the manner in which they fit together (i.e., order of crystallinity) are controlled by their chemical nature and the processing route. During the 1970s and 1980s considerable effort has gone towards realizing this potential in the simple linear polymer and impressive results have been obtained on a laboratory scale. Allied Corporation announced in the mid 1980s an extended chain ultrahigh molecular weight trade name with impressive properties.

In the mid 1970s reports of producing strong and stiff polyethylene fibers started to appear. Most of this work involved drawing of melt crystallized polyethylene to very high draw ratios. Tensile drawing, die drawing, or hydrostatic extrusion were used to obtain the high plastic strains required for obtaining a high modulus. Later developments have involved altogether different processing routes, two ways of achieving molecular orientation: a) without high molecular extension and b) with high molecular extension, resulted in moduli as high as 200 GPa. In all these methods, molecular orientation is achieved together with chain extension.

The chains are quite extended in this structure. A shish kebab structure consists of a continuous array of fibrous crystals, the shish kebabs, in which the molecular chains are highly extended. The third method of crystallization, and perhaps technologically the most important, leads to gels. Gels are nothing but swollen networks in which crystalline regions form the junctions. Essentially, an appropriate polymer solution is converted into gel which can be processed by a variety of methods to give the fiber. High molecular weight of the polymer and high concentration of the solution for a given molecular weight promote gel-forming crystallization. The alignment and extension of chains is obtained by the drawing of gel fiber. One problem with this gel route is the rather low spinning rates of 1.5 m/min. At higher rates, the properties obtained are not very good. Allied Corporation launched in the mid 1980s an UHMW-PE fiber, called Spectra 900, obtained by the gel processing route. Spectra 900 fiber is very light with a density of  $0.97 \text{ g cm}^{-3}$ . Its strength and modulus are slightly lower than those of aramid fibers but on a per unit weight basis, Spectra 900 has values about 30-40% higher than those of Kevlar. It should be pointed out that both these fibers as is true of most organic fibers, must be limited to low temperature applications. Spectra 900, for example, melts at  $150^\circ\text{C}$ . This solution spinning approach to producing high modulus and high strength fibers has been successfully applied in producing the aramid fibers. We describe these in the next section.

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## Aramid Fiber

Aramid Fiber is a generic name for a class of synthetic organic fibers called aromatic polyamide fibers. The U.S. Federal Trade Commission gives a good definition of an aramid fiber as "a manufactured fiber in which the fiber forming substance is a long chain synthetic polyamide in which at least 85% of the amide linkages are attached directly to two aromatic rings" Researchers at the Monsanto and Du Pont companies were independently able to produce high modulus aromatic fibers. Only Du Pont, however has produced them commercially under the trade name Kevlar since 1971.

Nylon is a generic name for any long chain polyamide. Aramid fibers like Nomex or Kevlar, however, are ring compounds based on the structure of benzene as opposed to linear compounds used to make nylon. The basic chemical structure of aramid fibers consists of oriented para-substituted aromatic units, which makes them rigid rodlike polymers. The rigid rodlike structure results in a high glass transition temperature and poor solubility, which makes fabrication of these polymers, by conventional drawing techniques, difficult. Instead, they are melt spun from liquid crystalline polymer solutions as described below.

**Fabrication:** Although the specific details of the manufacturing of aramid fibers remain proprietary secrets, it is believed that the processing route involves solution polycondensation of diamines and diacid halides at low temperatures. The most important point is that the starting spinnable solutions that give high strength and high modulus fibers have liquid crystalline order. Various states of polymer in solution depends on the type of polymer chain. Two-dimensional, linear, flexible chain polymers in solution are called random coils. If the polymer chain can be made of rigid units, that is, rodlike, they can be represented like a random array of rods. Any associated solvent may contribute to the rigidity and to the volume occupied by each polymer molecule. With increasing concentration of rodlike molecules, one can dissolve more polymer by forming regions of partial order, that is, regions in which the chains form a parallel array. This partially ordered state is called a liquid crystalline state. When the rodlike chains become approximately arranged parallel to their long axes but their centers remain unorganized or randomly distributed, we have what is called a nematic liquid crystal. It is this kind of order that is found in the extended chain polyamides.

Liquid crystal solutions, because of the presence of the ordered domains, are optically anisotropic, that is birefringent. The parallel array of polymer chains in the liquid crystalline state become even more ordered when these solutions are subjected to shear. It is this inherent property of liquid crystal solutions which is exploited in the manufacture of aramid fibers. The characteristic fibrillar structure of aramid fibers is due to the alignment of polymer crystallites along the fiber axis.

Organic Fibers Researchers at Du Pont discovered a spinning solvent for poly p-benzamide (PBA) and were able to dry spin quite strong fibers from tetramethylurea-LiCl solutions. This was the real breakthrough. The modulus of these as spun organic fibers was greater than that of glass fibers. p-Oriented rigid diamines and dibasic acids give polyamides that yield, under appropriate conditions of solvent, concentration, and polymer molecular weight, the desired nematic liquid crystal structure. One would like to have, for any solution spinning process a high molecular weight to obtain improved mechanical properties, a low viscosity to ease processing conditions, and a high polymer concentration to achieve a high yield. For para aramid, poly p-phenyleneterephthalamide (PPD-T), trade name Kevlar, the nematic liquid crystalline state is obtained in 100% sulfuric acid at a polymer concentration of about 20%. The polymer solution is often referred to as the dope. The various spinning processes available are classified as dry, wet and dry jet-wet spinning process. For aramid fibers, the dry jet wet spinning method is employed. It is believed that solution-polycondensation of diamines and diacid halides at low temperatures (near 0°C) gives the aramid forming polyamides. Low temperatures inhibit by product generation and promote linear polyamide formation. The resulting polymer is pulverized, washed, and dried. This is mixed with a strong acid (e.g., concentrated sulphuric acid) and extruded through spinnerets at 100 °C through about 1-cm air layer into cold water (0-4 °C). The fiber precipitates in the air gap and the acid is removed in the coagulation bath. The spinneret capillary and air gap cause rotation and alignment of the domains resulting in highly crystalline and oriented as-spun fibers.

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## Carbon Fibers

Carbon fibers are built by long carbon-carbon molecular chains yielding very stiff fibers. The trends have driven development of carbon fibers in two directions; high-strength (HS) fibers with very high tensile strength and a fairly high strain to failure (1-1.5%) and high modulus (HM) fibers with very high stiffness. Especially, the latter has found their use in advanced aerospace applications where the use of light weight materials with high stiffness is essential. Carbon fibers have a low coefficient of thermal expansion, good friction properties, good X-ray penetration and is non-magnetic. The main drawback is the high cost and all carbon composites are relatively brittle. The polyacrylonitrile fibers are stabilized in air (a few hours at 250 °C) to prevent melting during subsequent higher temperature treatment. The fibers obtained after this treatment are heated slowly in an inert atmosphere to 1000-1500 °C. Slow heating allows the high degree of order present in the fiber to be maintained. The rate of temperature increase should be low so as not to destroy the molecular order present in fibers. in air (a



few hours at 250 °C) to prevent melting during the subsequent higher-temperature treatment.

The initial stretching treatment of PAN improves the axial alignment of the polymer molecules. During the oxidation treatment the fibers are maintained under tension to keep the alignment of PAN while it transforms into rigid ladder polymer. In the absence of this tensile stress in this step, there will occur a relaxation and the ladder polymer structure will become disoriented. After the stabilization treatment, the resulting ladder type structure has high glass transition temperature so that there is no need to stretch the fiber during the next stage, namely carbonization. There still are present considerable quantities of nitrogen and hydrogen. These are eliminated as gaseous waste products during carbonization, that is heating to 1000-1500 degree C. The carbon atoms remaining after this treatment are in the form of a network of extended hexagonal ribbons. Although these strips tend to align parallel to the fiber axis, the degree of order of one ribbon with respect to another is relatively low. This can be improved by further heat treatment at still higher temperatures (upto 3000 °C). This is called the graphitization treatment. The mechanical properties of the resultant carbon fiber may vary over a large range depending mainly on the temperature of the final heat treatment. Hot stretching above 2000 °C results in plastic deformation of fibers leading to an improvement in properties.

## Cellulosic Precursors

Cellulose is a natural polymer and is frequently found in a fibrous form. In fact, cotton fiber, which is cellulosic, was one of the first ones to be carbonized. It has the desirable property of decomposing before melting. It is inappropriate, however, for high-modulus carbon fiber manufacture because it has a rather low degree of orientation along the fiber axis, although it is highly crystalline. It is also not available as a tow of continuous filaments and is quite expensive. These difficulties have been overcome in the case of rayon fiber, which is made from wood pulp, a cheap source. The cellulose is extracted from wood pulp and continuous filament tows are produced by wet spinning. Rayon is a thermosetting polymer. The process used for the conversion of rayon into carbon fiber involves the same three stages: stabilization in a reactive atmosphere (air or oxygen, <400 °C), carbonization (< 1500 °C), and graphitization (> 2500 °C). Various reactions occur during the first stage, causing extensive decomposition and evolution of H<sub>2</sub>, CO, CO<sub>2</sub>, and tar. The stabilization is carried out in a reactive atmosphere to inhibit tar formation and improve yield. Chain fragmentation or depolymerization occurs in this stage. Because of this depolymerization, stabilizing under tension, as done in the case of PAN precursor, does not work in this case. The carbonization treatment involves heating to about 1000 °C in nitrogen. Graphitization is carried out at 2800 °C but under stress. This orienting stress at high temperature results in plastic deformation via multiple slip system operation and diffusion. Figure 2.18 shows the process schematically. The carbon fiber yield from rayon is between 15 and 30% by weight compared to a yield of about 50% in the case of PAN precursors.

## Pitch-Based Carbon Fibers

There are various sources of pitch but the three commonly used sources are polyvinyl chloride (PVC), petroleum asphalt, and coal tar. Pitch-based carbon fibers have become attractive because of the cheap raw material and high yield of carbon fibers.

The same sequence of oxidation, carbonization, and graphitization is required for making carbon fibers out of pitch precursors. Orientation in this case is obtained by spinning. An isotropic but aromatic pitch is subjected to melt spinning at very high strain rates and quenched to give a highly oriented fiber. This thermoplastic fiber is then oxidized to form crosslinked structure that makes the fiber nonmelting. This is followed by carbonization and graphitization.

Commercial pitches are mixtures of various organic compounds with an average molecular weight between 400 and 600. Prolonged heating above 350 degree C results in the formation of a highly oriented, optically anisotropic liquid crystalline phase (mesophase). When observed under polarized light, anisotropic mesophase dispersed in an isotropic pitch appears as microspheres floating in pitch. The liquid crystalline mesophase pitch can be melt spun into a precursor for carbon fiber. The melt spinning process involves shear and elongation in the fiber axis direction and thus a high degree of preferred orientation is achieved. This orientation can be further developed during conversion to carbon fiber. The pitch molecules (aromatic of low molecular weight) are stripped of hydrogen and the aromatic molecules coalesce to form larger bidimensional molecules. Very high value of Young's modulus can be obtained. It should be appreciated that one must have the pitch in a state amenable to



spinning in order to produce the precursor fiber. This precursor fiber is made infusible to allow carbonization to occur without melting. Thus, the pitches obtained from petroleum asphalt and coal tar need pretreatments. This pretreatment can be avoided in the case of PVC by means of a carefully controlled thermal degradation of PVC. The molecular weight controls the viscosity of the melt polymer and the melting range. Thus, it also controls the temperature and the spinning speed. Because the pitches are polydispersoid systems, their molecular weights can be adjusted by solvent extraction or distillation.

## Structural Changes Occurring During Processing

The thermal treatments for all precursor fibers serve to remove non carbon elements in the form of gases. For this, the precursor fibers are stabilized (they become black) to ensure that they decompose before melting. Carbon fibers obtained after carbonization contain many growth defects because the thermal energy supplied at these low temperatures is not enough to break already formed carbon-carbon bonds. That is why these carbon fibers are very stable up to 2500-3000 °C when they change to graphite. The decomposition of the precursor fiber invariably results in a weight loss and a decrease in fiber diameter. The weight loss can be considerable - from 40 to 90% depending on the precursor and treatment. The external morphology of the fiber, however, is generally maintained. Thus, precursor fibers with transverse sections in the form of kidney bean, dog bone, or circle maintain this form after conversion to carbon fiber.

At the microscopic level, carbon fibers possess a rather heterogeneous microstructure. Many workers have attempted to characterize the structure of carbon fibers and there are in the literature a number of models. There exists a better understanding of the structure of PAN-based carbon fibers. Essentially a carbon fiber consists of many graphitic lamellar ribbons oriented roughly parallel to the fiber axis with a complex interlinking of layer planes both longitudinal and lateral.

## Properties and Applications

The density of the carbon fiber varies with the precursor and the thermal treatment given. It varies in the range of 1.6-2.2 g cm<sup>-3</sup>. Note that the density of the precursor being generally between 1.14 and 1.19 g cm<sup>-3</sup>. As mentioned above, the degree of order, and consequently the modulus in the fiber axis direction, increases with increasing graphitization temperature. Even among PAN carbon fibers we can have a series of carbon fibers: for example, high tensile strength but medium Young's modulus (HT) fiber (200-300 GPa); high Young's modulus (HM) fiber (400 GPa); extra- or superhigh tensile strength (SHT) and superhigh modulus type (SHM) carbon fibers. The mesophase pitch based carbon fibers show rather high modulus but low strength levels (2 GPa). Not unexpectedly, the HT type carbon fibers show a much higher strain to failure value than the HM type. The former are more widely used. The mesophase pitch based carbon fibers are used for reinforcement, while the isotropic-based fibers are more frequently used as insulation and fillers. For high-temperature applications involving carbon fibers, it is important to take into account the variation of inherent oxidation resistance of carbon fibers with modulus.

The carbon fibers produced from various precursor materials are fairly good electrical conductors. Although this had led to some work toward a potential use of carbon fibers as current carriers for electrical power transmission, it has also caused extreme concern in many quarters. The reason for this concern is that if the extremely fine carbon fibers accidentally become airborne (during manufacture or service) they can settle on electrical equipment and cause short circuiting.

Anisotropic as the carbon fibers are, they have two principal coefficients of thermal expansion, namely transverse or perpendicular to the fiber axis and parallel to the fiber axis. Carbon fibers have found a variety of application in the aerospace and sporting goods industries. Cargo bay doors and booster rocket casing in the US shuttle are made of carbon fiber reinforced epoxy composites. Modern commercial aircrafts also use carbon fiber reinforced composites. Among other areas of application of carbon fibers, one can cite various machinery items such as turbine, compressor, and windmill blades and flywheels; in the field of medicine the applications include both equipment as well as implant materials (e.g., ligament replacement in knees and hip joint replacement).

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## Boron Fibers

Boron is an inherently-brittle material. It is commercially made by chemical vapor deposition of boron on a substrate, that is, boron fiber as produced is itself a composite fiber. In view of the fact that rather high temperatures are required for this deposition process, the choice of substrate material that goes to form the core of the finished boron fiber is limited. Generally, a fine tungsten wire is used for this purpose. A carbon substrate can also be used. The first boron fibers were obtained by Weintraub by means of reduction of a boron halide with hydrogen on a hot wire substrate.

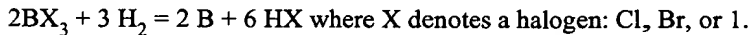
The real impulse in boron fiber fabrication, however, came only in 1959 when Talley used the process of halide reduction to obtain amorphous boron fibers of high strength. Since then, the interest in the use of strong but light boron fibers as a possible structural component in aerospace and other structures has been continuous, although it must be admitted that this interest has periodically waxed and waned in the face of rather stiff competition from other so-called advanced fibers, in particular, carbon fibers.

## Fabrication

Boron fibers are obtained by chemical vapor deposition (CVD) on a substrate. There are two processes:

**Thermal Decomposition of a Boron Hydride** This method involves low temperatures, and, thus, carbon coated glass fibers can be used as a substrate. The boron fibers produced by this method, however, are weak because of a lack of adherence between the boron and the core. These fibers are much less dense owing to the trapped gases.

**Reduction of boron Halide** : Hydrogen gas is used to reduce boron trihalide:



In this process of halide reduction, the temperatures involved are very high, and, thus, one needs a refractory material, for example, a high melting point metal such as tungsten, as a substrate. It turns out that such metals are also very heavy. This process, however, has won over the thermal reduction process despite the disadvantage of a rather high-density substrate (the density of tungsten is 19.3 g cm<sup>-3</sup>) mainly because this process gives boron fibers of a very high and uniform quality. There are many firms producing boron fibers commercially using this process.

In the process of BCl<sub>3</sub> reduction, a very fine tungsten wire (10-12 micron diameter) is pulled into a reaction chamber at one end through a mercury seal and out at the other end through another mercury seal. The mercury seals act as electrical contacts for resistance heating of the substrate wire when gases (BCl<sub>3</sub>, + H<sub>2</sub>,) pass through the reaction chamber where they react on the incandescent wire substrate. The reactor can be a one- or multistage, vertical or horizontal, reactor. BCl<sub>3</sub> is an expensive chemical and only about 10% of it is converted into boron in this reaction. Thus, an efficient recovery of the unused BCl<sub>3</sub> can result in a considerable lowering of the boron filament cost.

There is a critical temperature for obtaining a boron Fiber with optimum properties and structure. The desirable amorphous form of boron occurs below this critical temperature while above this temperature there occur also crystalline forms of boron that are undesirable from a mechanical properties viewpoint. With the substrate wire stationary in the reactor, this critical temperature is about 1000°C. In a system where the wire is moving, this critical temperature is higher and it increases with the speed of the wire. Fibers formed in the region above the dashed line are relatively weak because they contain undesirable forms of boron as a result of recrystallization. The explanation for this relationship between critical temperature and wire speed is that boron is deposited in an amorphous state and the more rapidly the wire is drawn out from the reactor, the higher the allowed temperature is. Of course, higher wire drawing speed also results in an increase in production rate and lower costs. Boron deposition on a carbon monofilament (-35 micron diameter) substrate involves precoating the carbon substrate by a layer of pyrolytic graphite. This coating accommodates the growth strains that result during, boron deposition.

## Structure and Morphology

The structure and morphology of boron fibers depend on the conditions of deposition: temperature, composition

of gases, gas dynamics, and so on. While theoretically the mechanical properties are limited only by the strength of the atomic bond, in practice, there always are present structural defects and morphological irregularities that lower the mechanical properties. Temperature gradients and trace concentrations of impurity elements inevitably cause process irregularities. Even greater irregularities are caused by fluctuations in electric power, instability in gas flow, or any other operator-induced variables.

## Structure

Depending on the conditions of deposition, the elemental boron has been observed in various crystalline polymorphs. The form produced by crystallization from the melt or chemical vapor deposition above 1300 degreeC is beta-rhombohedral. At temperatures lower than this, if crystalline boron is produced, the most commonly observed structure is alpha-rhombohedral. Boron fibers produced by the CVD method described above have microcrystalline structure that is generally called "amorphous". This designation is based on the characteristic X-ray diffraction pattern produced by the filament in the Debye-Scherrer method, that is, large and diffuse halos with d spacings of 0.44, 0.25, 0.17, 1.4, 1.1, and 0.091 nm, typical of amorphous material. Electron diffraction studies, however, lead one to conclude that this "amorphous" boron is really a microcrystalline phase with grain diameters of the order of 2 nm

Based on X-ray and electron diffraction studies. One can conclude that amorphous boron is really monocrystalline beta-rhombohedral. In practice, the presence of microcrystalline phases (crystals or groups of crystals observable in the electron microscope) constitutes an imperfection in the fiber that should be avoided. Larger and more serious imperfections generally result from surpassing the critical temperature of deposition or the presence of impurities in the gases. When boron fiber is made by deposition on a tungsten substrate, as is generally the case, then depending on the temperature conditions during deposition, the core may consist of, in addition to tungsten, a series of compounds, such as  $W_2$ , WB,  $W_2B_5$ , and  $WB_4$ . The various tungsten boride phases are formed by diffusion of boron into tungsten. Generally, the Fiber core consists only of  $WB_4$  and  $W_2B_5$ . On prolonged heating, the core may completely be converted into  $WB_4$ . As boron diffuses into the tungsten substrate to form borides, the core expands from its original 12.5 micron (original tungsten wire diameter) to 17.5 micron. The SiC coating is a barrier coating used to prevent any adverse reaction between B and the matrix such as Al at high temperatures. The SiC barrier layer is vapor deposited onto boron using a mixture of hydrogen and methylchlorosilane.

## Morphology

The boron fiber surface shows a "corn-cob" structure consisting of nodules separated by boundaries. The nodule size varies during the course of fabrication. In a very general way, the nodules start as individual nuclei on the substrate and then grow outward in a conical form until a filament diameter of 80-90 micron is reached, above which the nodules seem to decrease in size. Occasionally, new cones may nucleate in the material, but they always originate at an interface with a foreign particle or inclusion.

## Residual Stresses

Boron fibers have inherent residual stresses that have their origin in the process of chemical vapor deposition. Growth stresses in the nodules of boron, stresses induced by the diffusion of boron into the tungsten core, and stresses generated by the difference in the coefficient of expansion of deposited boron and tungsten boride core, all contribute to the residual stresses and thus can have a considerable influence on the fiber mechanical properties. The compressive stresses on the fiber surface are due to the quenching action involved in pulling the fiber out from the chamber. Morphologically, the most conspicuous aspect of these internal stresses would appear to be the frequently observed radial crack, from within the core to just inside the outer surface, in the transverse section of these fibers.

## Fracture Characteristics

It is well known that brittle materials show a distribution of strengths rather than a single value. Imperfections in these materials lead to stress concentrations much higher than the applied stress levels. Because the brittle material is not capable of deforming plastically in response to these stress concentrations, fracture ensues at one or more such sites. Boron fiber is indeed a very brittle material and cracks originate at preexisting defects located

at the boron-core interface or at the surface. As mentioned in the beginning, boron fiber in itself is a composite fiber. It is a consequence of the discontinuity between the properties of boron and tungsten borides. This discontinuity cannot be eliminated totally but can be minimized by a proper core formation and proper bonding between the core and the boron deposit.

## Properties and Applications of Boron Fibers

Due to the composite nature of the boron fiber, complex internal stresses and defects such as voids and structural discontinuities result from the presence of a core and the deposition process. Thus, one would not expect boron fiber strength to equal the intrinsic strength of boron. The average tensile strength of boron fiber is 3-4 GPa, while its Young's modulus is between 380 and 400 GPa.

An idea of the intrinsic strength of boron is obtained in a flexure test. It would be expected that in flexure, assuming the core and interface to be near the neutral axis, critical tensile stresses would not develop at the core or interface. Flexure tests on boron fibers lightly etched to remove any surface defects gave a strength of 14 GPa. Without etching the strength was half this value.

There has been some effort at NASA Lewis Research Center to improve the tensile strength and toughness (or fracture energy) of boron fibers by making them larger in diameter. Commercially produced 142-gm diameter boron fiber shows tensile strengths less than 3.8 GPa. The tensile strength and fracture energy values of the as-received and some limited-production run larger-diameter fibers showed improvement after chemical polishing. Fibers showing strengths above 4 GPa had their fracture controlled by a tungsten-boride core, while fibers with strengths of 4 GPa were controlled by fiber surface flaws. The high-temperature treatment, improved the fiber properties by putting a permanent axial contraction strain in the sheath.

Boron has a density of 2.34 g cm<sup>-3</sup> (about 15% less than that of aluminum). Boron fiber with the tungsten core has a density of 2.6 g cm<sup>-3</sup> for a fiber of 100 micron diameter. Its melting point is 2040 °C and it has a thermal expansion coefficient of  $8.3 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  up to 315 °C.

Boron Fiber composites are in use in a number of U.S. military aircraft, notably the F-14 and F-15, and in the U.S. Space Shuttle. Increasingly, boron fibers are being used for stiffening golf shafts, tennis rackets, and bicycle frames. One big obstacle to the widespread use of boron Fiber is its high cost compared to that of other fibers. A major portion of this high price is the cost of the tungsten substrate.

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